

2

AD-A202 999 PORT DOCUMENTATION PAGE

1a. SECURITY CLASSIFICATION AUTHORITY Unclassified		1b. RESTRICTIVE MARKINGS DTIC FILE COPY	
2a. SECURITY CLASSIFICATION AUTHORITY SELECTED		3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; distribution unlimited.	
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE 6 1989		5. MONITORING ORGANIZATION REPORT NUMBER(S) ARO 21763.2-EG	
4. PERFORMING ORGANIZATION REPORT NUMBER(S) D ^{CS}		7a. NAME OF MONITORING ORGANIZATION U. S. Army Research Office	
6a. NAME OF PERFORMING ORGANIZATION The Penn State University	6b. OFFICE SYMBOL (If applicable)	7b. ADDRESS (City, State, and ZIP Code) P. O. Box 12211 Research Triangle Park, NC 27709-2211	
6c. ADDRESS (City, State, and ZIP Code) The Pennsylvania State University University Park, PA 16802		9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER DAAG29-85-K-0042	
8a. NAME OF FUNDING/SPONSORING ORGANIZATION U. S. Army Research Office	8b. OFFICE SYMBOL (If applicable)	10. SOURCE OF FUNDING NUMBERS	
8c. ADDRESS (City, State, and ZIP Code) P. O. Box 12211 Research Triangle Park, NC 27709-2211		PROGRAM ELEMENT NO.	PROJECT NO.
		TASK NO.	WORK UNIT ACCESSION NO.
11. TITLE (Include Security Classification) The Effect of Platinum Catalysts on Propane Oxidation at Elevated Pressure			
12. PERSONAL AUTHOR(S) Wannam Lee, Thomas A. Litzinger, and Domenic A. Santavicca			
13a. TYPE OF REPORT Reprint	13b. TIME COVERED FROM TO	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
16. SUPPLEMENTARY NOTATION The view, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.			
17. COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)	
FIELD	GROUP	SUB-GROUP	
19. ABSTRACT (Continue on reverse if necessary and identify by block number) Abstract on Reprint			
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT <input type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS		21. ABSTRACT SECURITY CLASSIFICATION Unclassified	
22a. NAME OF RESPONSIBLE INDIVIDUAL		22b. TELEPHONE (Include Area Code)	22c. OFFICE SYMBOL

SAE Technical Paper Series

881614

The Effect of Platinum Catalysts on Propane Oxidation at Elevated Pressure

Wonnam Lee, Thomas A. Litzinger
and Domenic A. Santavicca

Pennsylvania State University

Accession For	
NTIS CRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By _____	
Distribution /	
Availability Codes	
Dist	Avail and/or Special
A-1	_____



International Fuels and Lubricants
Meeting and Exposition
Portland, Oregon
October 10-13, 1988

The appearance of the code at the bottom of the first page of this paper indicates SAE's consent that copies of the paper may be made for personal or internal use, or for the personal or internal use of specific clients. This consent is given on the condition, however, that the copier pay the stated per article copy fee through the Copyright Clearance Center, Inc., Operations Center, P.O. Box 765, Schenectady, N.Y. 12301, for copying beyond that permitted by Sections 107 or 108 of the U.S. Copyright Law. This consent does not extend to other kinds of copying such as copying for general distribution, for advertising or promotional purposes, for creating new collective works, or for resale.

Papers published prior to 1978 may also be copied at a per paper fee of \$2.50 under the above stated conditions.

SAE routinely stocks printed papers for a period of three years following date of publication. Direct your orders to SAE Order Department.

To obtain quantity reprint rates, permission to reprint a technical paper or permission to use copyrighted SAE publications in other works, contact the SAE Publications Division.



All SAE papers are abstracted and indexed in the SAE Global Mobility Database.

No part of this publication may be reproduced in any form, in an electronic retrieval system or otherwise, without the prior written permission of the publisher.

ISSN 0148-7191

Copyright ©1988 Society of Automotive Engineers, Inc.

Positions and opinions advanced in this paper are those of the author(s) and not necessarily those of SAE. The author is solely responsible for the content of the paper. A process is available by which discussions will be printed with the paper if it is published in SAE Transactions. For permission to publish this paper in full or in part, contact the SAE Publications Division.

Persons wishing to submit papers to be considered for presentation or publication through SAE should send the manuscript or a 300 word abstract of a proposed manuscript to: Secretary, Engineering Activity Board, SAE.

Printed in U.S.A.

The Effect of Platinum Catalysts on Propane Oxidation at Elevated Pressure

Wonnam Lee, Thomas A. Litzinger
and Domenic A. Santavicca

Pennsylvania State University

ABSTRACT

The potential for catalytically enhanced ignition in low-heat rejection Diesel engines has been experimentally studied under engine simulated conditions in a high pressure chemical flow reactor. Results are presented for propane oxidation on platinum at 6 and 10 atmospheres, at temperatures from 800K to 1050K, and at equivalence ratios from 0.5 to 4.0.

For turbulent transport rates which are typical of those in an engine, as much as 20% of the fuel was found to react on the catalyst before the onset of the gas-phase ignition reactions. Depending on the adiabaticity of the combustion chamber walls, this could lead to significant thermal enhancement of the gas-phase ignition process. Evidence of chemical enhancement was also observed, at 10 atm under very fuel rich conditions, in terms of a change in the concentration and distribution of the hydrocarbon intermediate species. Possible mechanisms for the observed chemical enhancement due to surface generated species are discussed. *Reprints. (25) ←*

THE USE OF IN-CYLINDER CATALYSTS to alter the combustion process in internal combustion (IC) engines has been proposed and studied by numerous researchers [1-5]. Diesel engine applications [1-4] have been motivated by the possibility of catalytically enhanced oxidation of both soot precursors and soot particles and thereby reduced particulate emissions. Spark ignition (SI) engine applications [4,5] have been motivated by the possibility that the catalyst would activate the charge prior to ignition and thereby extend the lean misfire limit and reduce cyclic variations. To date, however, results from engine tests have been inconclusive regarding the effects of in-cylinder catalysts. For example, in a Diesel engine with a platinum coated combustion chamber, Gaffney et al [1] reported a 40 percent reduction in soot emissions, while Siegl and Plee [2] observed essentially no difference between experiments with and without a platinum coated combustion chamber. Murray [4] evaluated the use of in-cylinder platinum catalysts in both SI and Diesel engines, and observed no, or perhaps a slightly negative, effect. In another study, Rychter et al [5] observed that the use of a catalyst in an SI engine resulted in the extension of the lean misfire limit and a significant reduction in the cycle to cycle pressure variations.

There are several reasons why it is difficult to evaluate the effects of in-cylinder catalysts from the results of these engine experiments. A common limitation of all the catalytic engine tests which have been reported to date is that the catalyst temperature has not been measured. The catalyst temperature required for catalytic effects to be important is not clear, but obviously the catalyst temperature should be above the catalytic ignition temperature in order to achieve significant catalytic effects. As a consequence, since the combustion chamber wall temperature in water-cooled IC engines is typically below 500 K and the catalytic ignition temperature for Diesel fuel in air over platinum is approximately 550 K [6], it is unreasonable to expect significant catalytic effects in water-cooled engines. Another limitation of some of the engine tests is the use of catalytic inserts [3], which alter the in-cylinder gas motion and make unambiguous determination of catalytic effects difficult, if not impossible. It should be noted that the practicality of using such inserts is also questionable. The most serious limitation of these engine tests, however, is the lack of fundamental information regarding both the nature and magnitude of catalytic effects under the high pressure, highly turbulent, transient conditions encountered in an engine. Obtaining this information should be considered a necessary first step in developing a catalytically enhanced IC engine. Such information will also be essential for evaluating and optimizing such an engine's performance. Therefore, the objective of this research has been to obtain fundamental information regarding the nature and magnitude of catalytic effects using a high pressure chemical flow reactor capable of simulating the combustion chamber flow field. In order to identify the relevant flow field parameters, however, one must first understand the basic nature of the catalytic combustion process.

The effect of catalytic surface reactions on the overall combustion process is determined by the relative rates of the gas-phase reactions, gas-phase diffusion, and surface reactions. Figure 1 shows the overall reaction rate for a catalytic combustion process as a function of temperature [7]. At low temperature (region 1), the reaction rate is controlled by the surface kinetics. As the temperature is increased (region 2), the surface reaction rate becomes so high that the overall process is limited by the rate of species transport between the bulk gas flow and the catalyst surface. This is known as the mass transfer limited regime. In the mass transfer limited

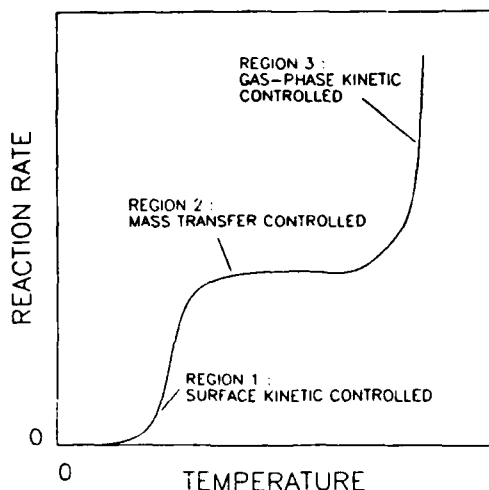


Figure 1. Overall reaction rate vs temperature for a typical catalytic combustion process.

regime, the overall reaction rate can not be increased significantly by increasing the catalyst's activity or temperature. Further increases in the temperature will eventually lead to the initiation of gas-phase reactions (region 3), after which the overall reaction rate becomes controlled by the homogeneous gas-phase reactions, and therefore again increases rapidly with increasing temperature.

Based on this understanding of the catalytic combustion process, it is clear that there are two important aspects to consider with respect to the potential use of in-cylinder catalysts. The first is that for catalytic effects to be significant the temperature of the catalyst must be greater than the catalytic ignition temperature, while the gas temperature should not be so high that the gas-phase reactions dominate. This suggests that the most likely part of the combustion process to be affected by in-cylinder catalysts is the ignition chemistry, since after gas-phase ignition has occurred the gas-phase reactions will dominate. These considerations define the temperature range of interest to be between approximately 550 K and 1100 K. The lower limit, which depends on the catalytic ignition temperature, will vary with the catalyst and fuel. The upper limit, which depends on the gas-phase ignition temperature, will vary with fuel type and pressure. Therefore, it is also important that the effects of fuel type, catalyst, and pressure be studied as well. The second important consideration is that in this temperature regime, the overall reaction rate will be limited by the mass transport rate of the system, and therefore, the flow characteristics are important in determining the effect of the catalytic surface reactions. In particular, the high turbulence levels which are typical of engine flow fields must be simulated in the flow reactor experiment since the resultant turbulent transport is likely to enhance the effectiveness of the mass transport limited catalyst.

These considerations therefore lead to the conclusion that the use of in-cylinder catalysts can be expected to have the greatest impact on the ignition characteristics of low-heat rejection Diesel engines, where the parameters of importance include the gas temperature, catalyst temperature, pressure, turbulence intensity and scale, reaction time, fuel type, and catalyst type. Therefore, in the flow reactor experiments it is important that the

effects of these parameters be studied over a range of conditions which are typical of those in low-heat rejection Diesel engines near top dead center.

The results presented in this paper are for propane fuel and platinum (Pt) catalysts. Although platinum is an unlikely candidate for actual engine applications, because of its expense and limited high temperature durability, it is an excellent hydrocarbon oxidation catalyst for which the catalytic surface reactions are relatively well understood. Similarly, propane is not a typical Diesel fuel, however its gas-phase and catalytic (Pt) oxidation chemistry are relatively well understood. Therefore, the choice of propane and platinum was made to facilitate the interpretation of the results, as well as to provide a valuable reference case for future tests involving higher molecular weight fuels and ceramic catalysts.

Propane oxidation on platinum has been studied by numerous researchers [e.g., 8,9,10]. Most of this work has been conducted under fuel lean conditions, where the major products are carbon dioxide and water [8,9]. The production of these species yields significant chemical heat release which, if effectively transported back to the gas flow, may lead to thermal enhancement of the gas-phase chemistry. It should be noted, however, that under fuel rich conditions, Marteney et al [10] observed a competition between carbon dioxide and carbon monoxide production where the carbon monoxide concentration increases with increasing equivalence ratio and thereby reduces the chemical heat release.

It has also been suggested [11] that the catalyst may act as a source of radical species which diffuse into the gas-phase and lead to a chemical enhancement of the gas-phase chemistry. In order to study possible chemical enhancement of the gas-phase chemistry by surface generated radicals, it is important to first understand the basic characteristics of the gas-phase ignition chemistry. Propane gas-phase ignition chemistry has been studied and reasonably well characterized at atmospheric pressure. Some of the fundamental characteristics of the chemical processes may change at elevated pressure [12], however, phenomenologically the ignition chemistry should be the same. Westbrook and Pitz [13] have developed a comprehensive model of propane oxidation chemistry. The principal fuel consumption route is hydrogen atom abstraction to form an iso- or normal propyl radical, primarily the result of reaction with H, O and OH. Depending on the concentrations of H, O and OH, the relative concentrations of iso- and normal propyl radicals will change.

During the early portion of the reaction when intermediate concentrations are small, production dominates over consumption of these species. In this phase, the most important reactions for the production of intermediate hydrocarbons are:



Since the concentrations of iso- and normal propyl radicals depend on the concentrations of H, O and OH, reactions 1 - 7 show that the intermediate hydrocarbon product distribution can change as a result of a change in the concentration of H, O or OH radicals.

Several experiments [14-17] have shown that OH radicals can be desorbed from a platinum surface exposed to hydrogen/oxygen mixtures at temperatures above 1100 K. Recently, Pfefferle et al [14] observed O radical desorption, as well as OH radical desorption, from a platinum surface exposed to methane/air and ethane/air mixtures at temperatures above 1500K. The conditions used in these studies were relatively high temperature, fuel lean, and atmosphere or lower pressure. Fuel rich and high pressure conditions, however, may change the catalytic reaction mechanism and radical desorption characteristics. Marteney et al [10] showed that the catalytic reaction mechanisms change under fuel rich conditions for propane/air mixtures on platinum; similarly, Hanson and Boudart [18] proposed two different reaction schemes for fuel rich and fuel lean hydrogen oxidation over Pt/SiO₂ catalysts. There is, however, no direct evidence of radical production by catalytic surface reactions under fuel rich conditions. Another factor which might be considered, particularly under fuel rich conditions, is the possible direct production of partially oxidized or pyrolyzed species by catalytic surface reactions [19].

As noted previously, the primary objective of this study is to determine whether or not in-cylinder catalysts can be used to enhance the ignition characteristics of low-heat rejection Diesel engines. In order to predict the effect of in-cylinder catalysts, an understanding of the nature and magnitude of catalytic effects under the high pressure, transient, turbulent flow conditions found in the combustion chamber of an engine is necessary. Such information, however, is not available and is unlikely to be obtained from

experiments conducted in an actual engine due to the complex and interdependent nature of the engine combustion process. Therefore, experiments have been conducted in a high pressure chemical flow reactor which is capable of simulating engine flow field conditions, while clearly isolating the effects of catalytic surface reactions. The experiments were conducted under nearly isothermal conditions in order to study both thermal and chemical enhancement of the gas-phase ignition chemistry. The experiments were conducted both with and without the catalyst, and the gas-phase chemistry was monitored using conventional gas sampling and chemical analysis techniques. Catalytic effects were evidenced by changes in the intermediate hydrocarbon concentrations between the catalytic and non-catalytic tests.

EXPERIMENTAL DESCRIPTION

A high pressure chemical flow reactor, shown schematically in Figure 2, was designed and constructed for the study of catalytic and gas-phase reactions at pressures up to 20 atmospheres and temperatures up to 1100 K. The flow reactor was operated with oxidant supplied by independently metered oxygen and nitrogen gas supplies. In order to reduce the reaction rate and limit the temperature rise along the length of the test section, experiments were conducted with 2 percent oxygen. The equivalence ratio used in this study was therefore based on the fuel to oxygen ratio. The oxidant was heated with electric heaters to the desired temperature and passed through the fuel-air mixing section, where gaseous or vaporized liquid fuel was injected and mixed with the preheated oxidant.

A critical part of any chemical flow reactor is the fuel-air mixing section. Rapid and complete mixing is essential in order to minimize chemical reactions in the mixing section. The mixing section used in this study

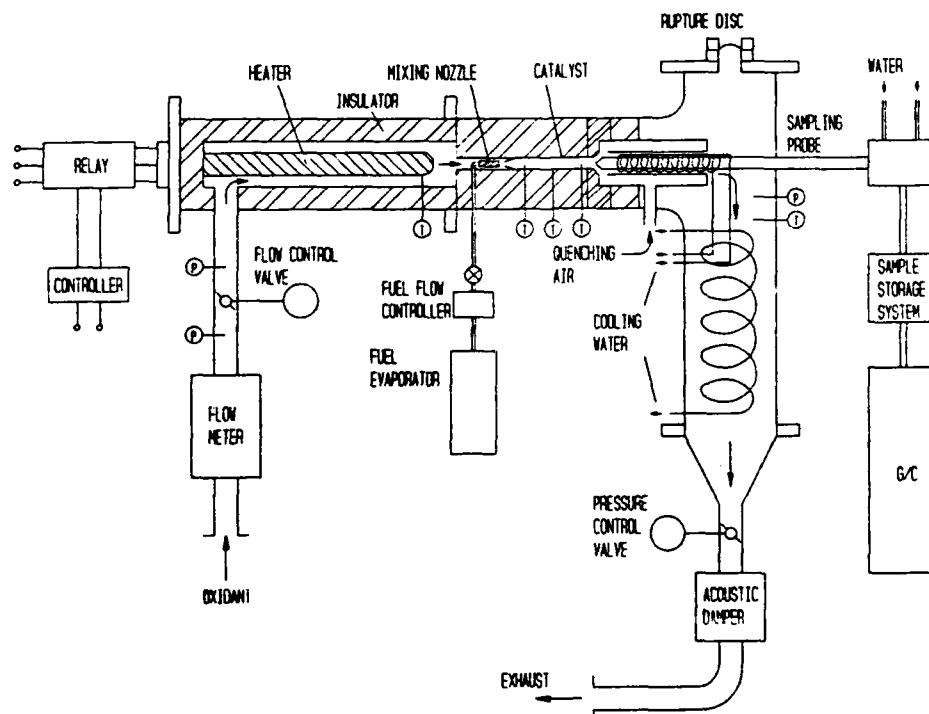


Figure 2. High pressure chemical flow reactor.

relied on transverse fuel injection, followed by rapid turbulent mixing in a number of small diameter passageways (Figure 3). The fuel-air mixture then entered the test section through high velocity, radially opposed jets which generated the desired turbulence conditions. The residence time in the mixing section was less than 10 percent of the residence time in the test section. Also, nitrogen dilution of the fuel was used to reduce the residence time in the high temperature sections of the fuel delivery lines in order to avoid pyrolysis of the fuel before it reached the mixing section. The test section used in this study was 7.8 mm in diameter and 100 mm long, and was selected to match typical surface to volume ratios in direct injection Diesel engine combustion chambers near top dead center. A stainless steel test section was used for the gas-phase or non-catalytic experiments, which served as a reference case for the catalytic experiments. A platinum coated stainless steel test section (supplied by W. B. Retallick) was used for the catalytic tests.

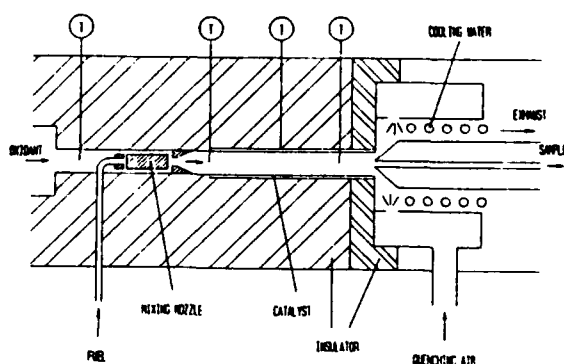


Figure 3. test section.

The gas temperature was measured near the entrance and exit of the test section by chromel-alumel thermocouples which were inserted directly into the flow. The catalyst temperature was measured at several locations along the length of the test section by thermocouples attached directly to the outside of the test section. Reaction products were sampled at the exit of the test section with a temperature controlled sampling probe. The samples were stored in a multi-position sampling valve, and then analyzed by gas chromatography. Immediately downstream of the sampling probe entrance, the combustion gases were diluted and quenched in order to avoid possible explosion.

Experiments were conducted by fixing the fuel to oxygen ratio, pressure, and test section residence time and varying the temperature. Using oxidant with an oxygen concentration of 2 percent, the flow reactor was initially preheated to the desired temperature. Once the temperature reached steady state, propane was injected into the mixing section and reaction products were extracted at the exit of the test section with the sampling probe. After obtaining a sample, the temperature was increased and when steady state was re-established, the fuel injection and sampling procedure was repeated. Gas and surface temperatures were measured at the same time that the reaction products were sampled. The insulated test section was not perfectly isothermal due to heat loss through the test section walls and heat release from the chemical reactions. The temperature difference between the gas temperature at the entrance and exit of the test section was typically less than 20 K. The gas

temperature, therefore, was defined as the average of the gas temperatures at the entrance and exit of the test section.

The same procedure was used for the catalytic tests, however, because of the significant fuel conversion on the catalytic surface, it was necessary to extract a gas sample and measure the catalyst and gas temperatures between 5 and 15 seconds after the start of fuel injection. This was sufficiently long to achieve quasi-steady state conditions in the test section [20] and short enough to keep typical catalyst temperature rise to less than 20K.

Experiments were conducted at 6 and 10 atmospheres, with a 10 millisecond residence time, and with equivalence ratios from 0.5 to 4.0. The concentrations of CO, CO₂, CH₄, C₂H₄, C₂H₆, C₃H₈ and C₃H₆ were determined by gas chromatography. By comparing the catalytic and non-catalytic measurements obtained at the same conditions, it was possible to evaluate the effect of the catalytic surface reactions on the gas-phase chemistry.

As discussed previously, free-stream turbulence is expected to play an important role in enhancing the effect of the catalytic surface reactions by increasing the mass transport between the catalytic surface and the bulk gas flow. Therefore, it was important to reproduce the turbulence intensities and length scales found in an engine. The turbulence generated in the flow reactor by the mixing section was characterized using a two-color laser Doppler velocimetry (LDV) system. The two-color LDV system used in this study was developed specifically for making two-point spatial correlation measurements from which the turbulence length scale can be calculated. The details of this LDV system are discussed by Wilson [21].

A Pyrex test section provided the optical access necessary to measure the flow properties at room temperature and atmospheric pressure. To simulate the actual flow conditions, the Reynolds number was set to match that at 1000 K and 10 atmospheres. Mean velocities and turbulence intensities were measured at four axial positions along the center line of the test section. However, because of particle seed deposition on the Pyrex tube, the integral length scale measurement was made 2mm downstream of the tube exit. Radial profiles of the mean velocity and turbulence intensity were also measured 2mm downstream of the tube exit.

The axial profiles of the mean velocity and turbulence intensity show the developing nature of the turbulent flow, where the mean velocity of the core flow increases from 10 m/s to 12.5 m/s and the turbulence intensity decays from 4.2 m/s to 0.9 m/s. These values are typical of those which have been measured in open chamber engines with swirl [22]. Radial profiles of the mean velocity and turbulence intensity measured at the exit of the test section are found to be relatively flat over the core region of the test section (Figure 4), indicating that the free stream turbulence penetrates nearly all the way to the test section wall. Again, this is typical of what have been observed in engine flow fields [22].

The turbulent transport depends on the turbulence intensity and length scale. The length scale was determined from the lateral spatial correlation coefficient at the test section exit measured by simultaneous, two-point velocity measurements at various separations. The lateral length scale is equal to the area under the spatial correlation curve. The resultant integral length scale is 0.8 mm, which is approximately 10 percent of the test section diameter. This length scale is comparable to those which have been measured in an engine [23], therefore, the turbulent flow

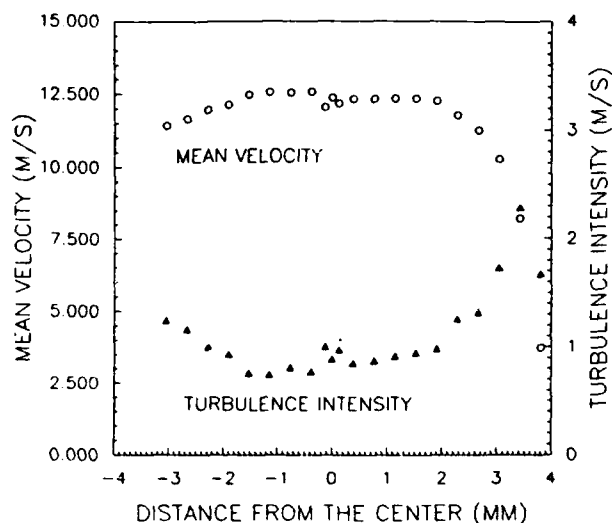


Figure 4. Profiles of mean velocity and turbulence intensity vs radial position.

in the test section, both in terms of its intensity and scale, can be considered similar to that found in an actual engine.

RESULTS AND DISCUSSION

Fuel conversion as a function of temperature is shown in Figure 5 for the 6 atmosphere catalytic tests, with 2 percent oxygen and an equivalence ratio of 3.0. These results clearly illustrate the three regimes of catalytic combustion which were discussed previously. At low temperatures, the overall reaction rate is surface kinetics controlled, however, as the temperature, and in turn the surface reaction rate, increases the overall reaction rate becomes mass transport limited. The transition temperature between the surface kinetic and the mass transport limited regimes is approximately 575K for this case. Within the mass transport limited regime, the overall reaction rate only increases marginally with increasing catalyst temperature. At approximately 950K, however, the onset of gas-phase reactions is evidenced by a marked increase in fuel conversion with increasing temperature. At temperatures above 950K, which is effectively the gas-phase ignition temperature, the gas-phase reactions rapidly begin to dominate the overall fuel conversion. Similar behavior was observed for equivalence ratios of 0.5 and 1.0 and at 10 atmospheres.

Two important observations can be made from these results regarding potential engine applications. One is that the catalyst temperature, for propane fuel and platinum catalysts, should be at least 575K to achieve maximum catalytic effects. Higher surface temperatures, however, are not necessary since the effectiveness of the catalyst is mass transport limited. A second observation is that approximately 10 to 20 percent of the fuel reacts on the catalyst prior to the onset of the gas-phase ignition reactions. Since the catalyst converts the fuel directly to CO_2 and H_2O under fuel lean conditions and to CO , CO_2 and H_2O under fuel rich conditions, there will be significant heat release associated with the catalytic reactions. Depending on the adiabaticity of the combustion chamber wall and the

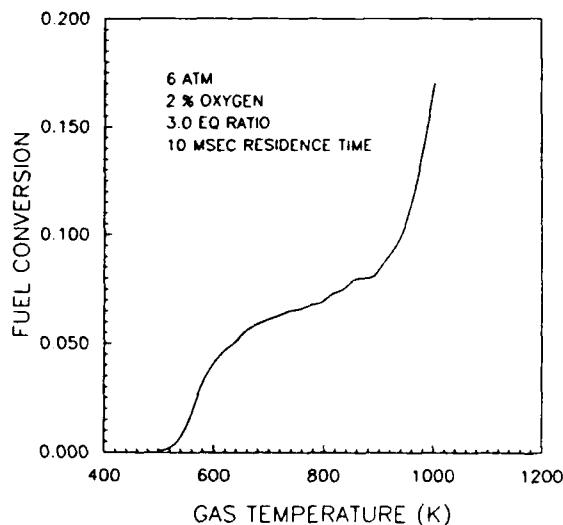


Figure 5. Fuel conversion vs temperature for catalytic test.

turbulent transport rates, this could result in preheating of the fuel-air mixture and thereby lead to significant thermal enhancement of the gas-phase ignition chemistry.

As discussed previously, both thermal and chemical enhancement of the gas-phase ignition chemistry is possible. In order to detect the possibility of chemical enhancement, experiments were conducted under the same conditions but without the platinum catalyst. In this case, it should be noted that due to the high turbulent transport rates and the large surface to volume ratio, that radical recombination reactions on the stainless steel walls of the test section are likely to have an effect on the gas-phase chemistry. This is, however, still a reasonable, and in fact the most appropriate, comparison in order to understand the potential effects of in-cylinder catalysts. If the catalyst does serve as a source of either radical or stable intermediate species, their effect on the gas-phase ignition chemistry should be evidenced by changes in the concentration and distribution of the intermediate hydrocarbon species that are measured after the onset of the gas-phase reactions.

Figures 6 and 7 show normalized species concentrations for the non-catalytic and the catalytic tests, respectively, at 10 atmospheres and an equivalence ratio of 4.0. Normalized concentration is defined as the species concentration divided by the initial fuel concentration. These results are typical of those obtained at all conditions tested where the most apparent difference between the two cases is the significant amount of carbon monoxide and carbon dioxide which is produced catalytically.

The effect of the catalyst is clearly shown in Figures 8 and 9, where the normalized total intermediate hydrocarbon concentration is plotted versus inverse temperature for 10 atmospheres and equivalence ratios of 1.0 and 4.0, respectively. Both the catalytic and the non-catalytic results are presented, as well as the difference between the two, which is representative of the effect of the catalytic surface reactions on the gas-phase ignition chemistry. Figure 8 shows that there is no significant change in the production of intermediate hydrocarbons due to the catalyst at 10 atmospheres and an equivalence ratio of 1.0. Similarly, no significant

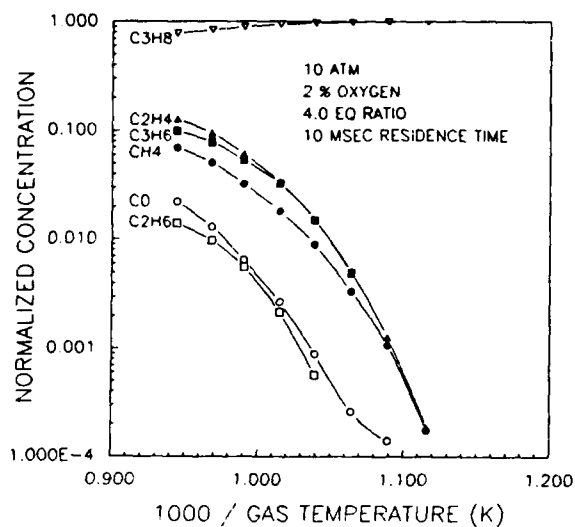


Figure 6. Product distribution vs inverse temperature for non-catalytic test.

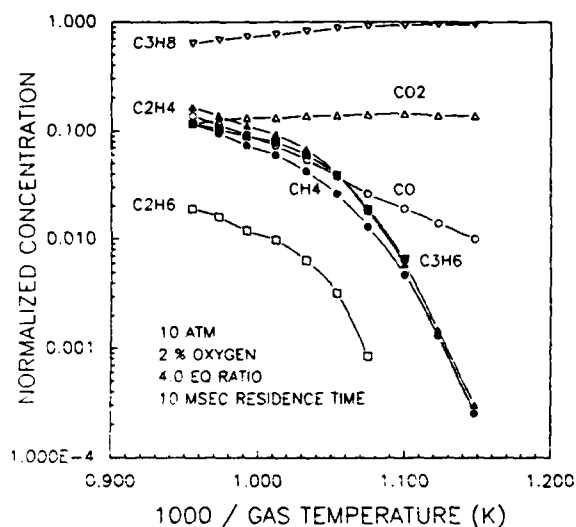


Figure 7. Product distribution vs inverse temperature for catalytic test.

difference was observed at 6 atmospheres and equivalence ratios of 0.5, 1.0 and 3.0. The only case for which a significant difference was observed was at 10 atmospheres and an equivalence ratio of 4.0 as shown in Figure 9. If the gas-phase ignition temperature is defined, for example, as the temperature at which 1 percent of the fuel is converted into intermediate hydrocarbons, these results indicate that the catalyst lowers the gas-phase ignition temperature from approximately 935 K to 900 K for these particular conditions. Figure 9 also shows that the difference in the total intermediate hydrocarbons between the catalytic and the non-catalytic cases increases with increasing temperature up to 990 K, after which it remains approximately constant with increasing temperature. There are two possible explanations for this behavior. One is that the mechanism by which the catalyst

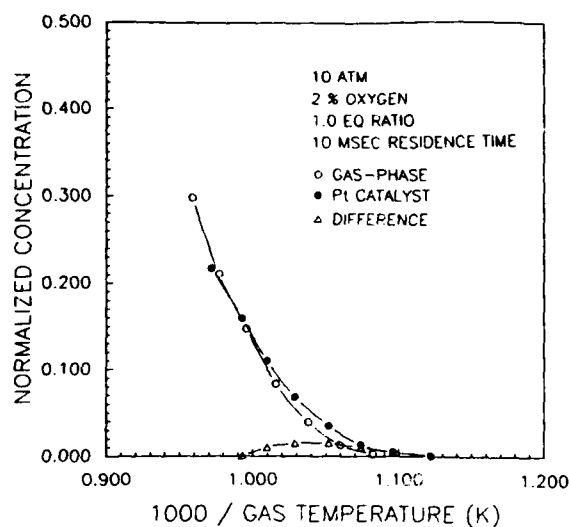


Figure 8. Normalized total intermediate hydrocarbons vs inverse temperature.

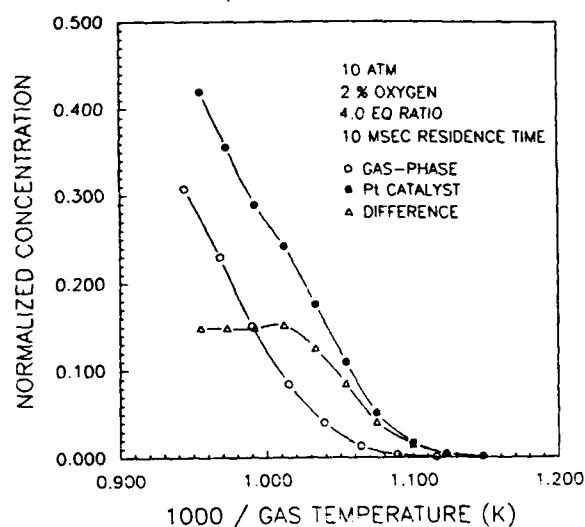


Figure 9. Normalized total intermediate hydrocarbons vs inverse temperature.

enhances the gas-phase production of intermediate hydrocarbons becomes mass transport limited above 990 K. The second is that gas-phase consumption of the intermediate hydrocarbons is beginning to become important and is acting to cancel the increasing catalytic effects. Unfortunately, it is not possible from these measurements to ascertain the correct explanation for this behavior.

Another important question is whether the increased intermediate hydrocarbon concentrations are due to a change in the gas-phase chemistry caused by surface generated radicals or to the fact that they are produced directly by the catalyst. In order to address this question, the percentage of the intermediate hydrocarbon species is plotted versus inverse temperature for 10

atmospheres and equivalence ratios of 1.0 and 4.0 in Figures 10 and 11, respectively. Both the catalytic and the non-catalytic results are presented. In these Figures, percentage is defined with respect to the total intermediate hydrocarbons. The results in Figure 11 for 10 atmospheres and an equivalence ratio of 4.0 show a distinct change in the product distribution due to the catalytic effects. Specifically, the percentages of methane and ethane increase and of ethylene and propylene decrease in the catalytic case. Figure 10 also appears to show some evidence of catalytic effects at 10 atmospheres and an equivalence ratio of 1.0 in terms of a small increase in methane and decrease in ethylene concentration, even though the total intermediate hydrocarbon concentration, shown in Figure 8, does not change significantly.

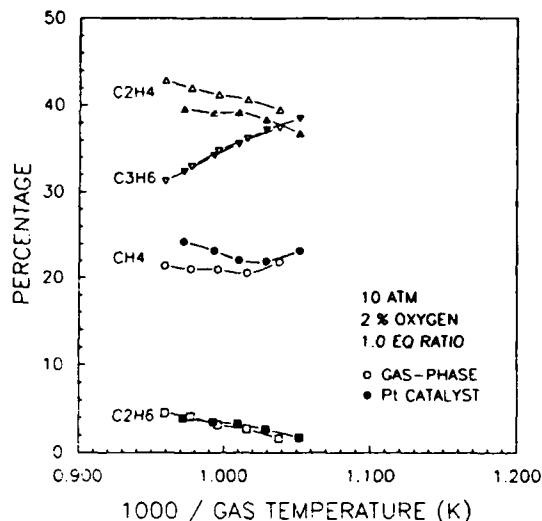


Figure 10. Relative concentrations of intermediate hydrocarbons vs inverse temperature.

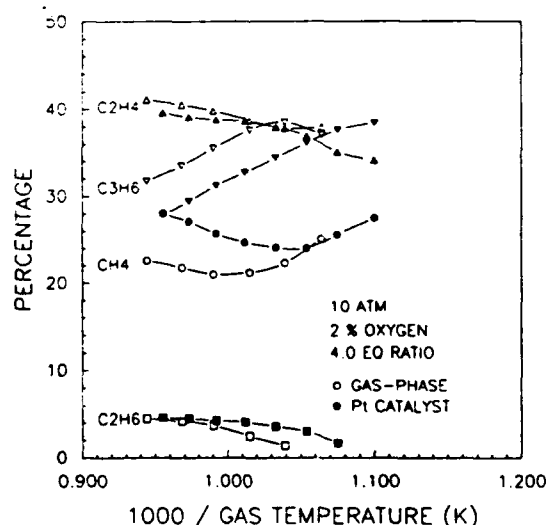


Figure 11. Relative concentrations of intermediate hydrocarbons vs inverse temperature.

The observed changes in product distribution could result from surface generated radicals or stable products. Regarding the possible role of surface generated radicals, reactions 5, 6 and 7 indicate that an increased methyl radical concentration could explain the observed increase in methane and ethane production. Similarly, the decrease in propylene compared to ethylene suggests that there is an increase in normal propyl relative to isopropyl radicals (reactions 1-4), which could be attributed to greater concentrations of the more selective H-atoms and methyl radicals [13]. An alternative possibility is that hydrocarbon intermediates are produced directly on the catalyst. It is known [24] that unsaturated hydrocarbon molecules, e.g. ethylene and propylene, are more readily adsorbed on platinum than are saturated hydrocarbons, e.g. methane and ethane. This implies that methane and ethane would be more readily desorbed which is consistent with the observed proportionately greater increase in methane and ethane. Unfortunately, the relative importance of radical or stable species generation for chemical enhancement of the gas-phase chemistry can not be established based on current results.

CONCLUSIONS

Under engine simulated flow field conditions, for the case of propane fuel and platinum catalysts, 10 to 20 percent of the fuel is converted to CO₂, H₂O and CO prior to the onset of significant gas-phase reactions. Depending on the adiabaticity of the combustion chamber walls, the heat generated by this fuel conversion could serve to preheat the fuel-air mixture and thereby thermally enhance the gas-phase ignition process. For propane fuel and platinum catalysts, chemical enhancement of the gas-phase ignition chemistry was also observed, but only for 10 atmospheres and very fuel rich equivalence ratios. This was evidenced by an increase in the fuel conversion to intermediate hydrocarbons as well as by a change in the intermediate hydrocarbon product distribution. From these measurements however, it is not clear whether this is due to surface generated CH₃ and/or H radicals or to the fact that the intermediate hydrocarbons are produced directly by the catalytic surface reactions. The effect of the observed chemical enhancement was a measurable decrease in the gas-phase ignition temperature, which for the particular conditions of these tests was approximately 35 K. These results are quite promising with respect to the potential use of in-cylinder catalysts to improve the ignition characteristics of low cetane number fuels.

ACKNOWLEDGEMENT

This work was supported by the Army Research Office under contract No. DAAG29-85-K-004A.

REFERENCES

1. Gaffney, J., Sapienza, R., Butcher, T., Krishna, C., Marlow, W., and O'Hare, T., "Soot Reduction in Diesel Engines: A Chemical Approach," Comb. Sci. and Tech., Vol. 24, 89-92 (1980).
2. Siegl, D. and Plee, S. L., "Heterogeneous Catalysis in the Diesel Combustion Chamber," Comb. Sci. and Tech., Vol. 27, 97-102 (1982).

3. Thring, R. H., "The Catalytic Engine - Platinum Improves Economy and Reduces Pollutants from a Range of Fuels," *Platinum Metals Review*, Vol. 27, 4, 126-133 (1980).
4. Murray, R. G., "Performance & Emission Characteristics of a Semi-Adiabatic Engine," ASME Technical Paper 80DGP-44 (1980).
5. Rychter, T. J., Saragih, R., Lezanski, T., and Wojcicki, S., "Catalytic Activation of a Charge in a Prechamber of a SI Lean-Burn Engine," Eighteenth Symposium (International) on Combustion, 1815-1824 (1981).
6. Heck, R. M., Chang, M., Hess, H., and Carrubba, R., "Durability Testing at One Atmosphere of Advanced Catalysts and Catalyst Supports for Automotive Gas Turbine Engine Combustors," NASA CR-135132, June 1977.
7. Trimm, D. L., "Catalytic Combustion (Review)," *Applied Catalysis*, Vol. 7, 249-282 (1983).
8. Hiam, L., Wise, H., and Chaikin, S., "Catalytic Oxidation of Hydrocarbons on Platinum," *J. of Catalysis*, 9, 10, 272-276 (1968).
9. Schwartz, A., Holbrook, L. L. and Wise, H., "Catalytic Oxidation Studies with Platinum and Palladium," *J. of Catalysis*, 21, 199-207 (1971).
10. Marteney, P. J. and Kesten, A. S., "Kinetics of Surface Reactions in Catalytic Combustion," Eighteenth Symposium (International) on Combustion, 1899-1908 (1981).
11. Pfefferle, L. D., Pfefferle, W. C., "Catalysis in Combustion," *Catal. Rev.-Sci. Eng.*, 29(2&3), 219-267 (1987).
12. Lee, W., Hoffman, J., Litzinger, T. A., Santavicca, D. A., and Pitz, W. J., "Oxidation of Propane at Elevated Pressures - Experiments and Modelling," in preparation (1988).
13. Westbrook, C. K. and Pitz, W. J., "A Comprehensive Chemical Kinetic Reaction Mechanism for Oxidation and Pyrolysis of Propane and Propene," *Comb. Sci. and Tech.*, Vol. 37, 117-152 (1984).
14. Pfefferle, L. D., Griffin, T. A., Crosley, D. R. and Dyer, M. J., "Ignition of Ethane/Methane Mixtures Over Heated Quartz and Platinum Surfaces," 22nd Symposium (Int'l.) on Combustion, Seattle, WA (1988).
15. Fujimoto, G. T., Selwyn, G. S., Keiser, J. T., and Lin, M. C., "Temperature Effect on the Removal of Hydroxyl Radicals by a Polycrystalline Platinum Surface," *J. Phys. Chem.*, 87, 1906-1910 (1983).
16. Tevault, D. E., Tally, L. D., and Lin, M. C., "Matrix Isolation and Laser Diagnostic Studies of Catalytic Oxidation of H_2 and D_2 on Platinum," *J. Chem. Phys.*, 72(5), 3314-3319 (1980).
17. Talley, L. D., Sanders, W. A., Bogan, D. J., and Lin, M. C., "Internal Energy of Hydroxyl Radicals Desorbing from Polycrystalline Pt Surfaces," *Chemical Physics Letters*, 78(3), 500-503 (1981).
18. Hanson, F. V. and Boudart, M., "The Reaction between H_2 and O_2 over Supported Platinum Catalysts," *J. of Catalysts*, 53, 56-67 (1978).
19. Brabbs, T. A. and Olson, S. L., "Fuel-Rich Catalytic Combustion - A Soot-Free Technique for In Situ Hydrogen-like Enrichment," NASA Technical Paper 2498, 1985.
20. Sinha, N., Bruno, C. and Bracco, F. V., "Two-Dimensional, Transient Catalytic Combustion of CO/Air on Platinum," *Physico-Chemical Hydrodynamics*, Vol. 6, No. 4, pp. 373-391 (1985).
21. Wilson, C. "Length Scale Measurement Techniques: For the Study of Premixed Turbulent Flames" MS Thesis, Mechanical Engineering Department, Pennsylvania State University, 1988.
22. Hall, M. J. and Bracco, F. V., "A Study of Velocities and Turbulence Intensities Measured in Firing and Motored Engines," SAE Paper 870453, 1987.
23. Fraser, R. A. and Bracco, F. V., "Cycle-Resolved LDV Integral Length Scale Measurements in an I.C. Engine," SAE Paper 880381, 1988.
24. Cho, P. and Law, C. K., "Catalytic Ignition of Fuel/Oxygen/Nitrogen Mixtures over Platinum," *Combustion and Flame*, Vol. 66, 159-170 (1986).